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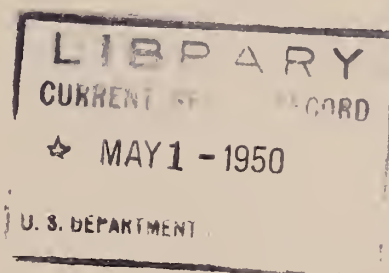
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³ PROPERTIES OF ALLYLSUCROSE AND ALLYLSUCROSE COATINGS

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PROPERTIES OF ALLYLSUCROSE AND ALLYLSUCROSE COATINGS

Morris Zief¹ and E. Yanovsky²

Introduction

Sucrose (beet or cane sugar) is manufactured in a substantially pure condition and in quantities far greater than any other organic chemical. In 1947 the total world production of sugar from sugar cane and beets was 28,600,000 metric tons (1). Sucrose is utilized almost exclusively as food. Although consumption of sugar in some countries is rather low, frequent surpluses of this commodity occur on the international market. Thus far, efforts to find nonfood applications for sugar have been largely unsuccessful, and large-scale utilization of this inexpensive and abundant chemical remains an outstanding challenge to the imagination and ingenuity of chemists and technologists.

The only derivative of sucrose made on a limited industrial scale is sucrose octaacetate, which is used as a denaturant of alcohol, a plasticizer, and an ingredient in adhesives. Sucrose octanitrate has probably been used at various times as an explosive. Many other derivatives of sucrose (particularly esters and ethers) have been prepared, but with the exception of sucrose octaacetate none has achieved practical importance.

In 1923 Tomecko and Adams (2) described the preparation of unsaturated (allyl) ethers of several carbohydrates. In 1945 the compounds described by Tomecko and Adams and a number of other polyhydroxy compounds were made by improved preparative methods (3). It was found that many of these allyl ethers can be polymerized to insoluble resins - a fact overlooked by most of previous investigators - thus opening a new chapter in the rapidly developing field of plastics.

The allyl ethers can apparently be used for coatings and other practical applications. Although all allyl ethers studied are somewhat similar, they are by no means identical. The practical use of each will depend on its specific properties and, of course, on economic considerations, that is cost of production. One such promising compound - allyl starch - has been described in a number of publications (4, 5, 6, 7). This paper describes the preparation, properties and potential uses of another promising allyl ether - allylsucrose. This compound shows promise of becoming the most direct outlet for large-scale industrial utilization of sucrose.

Preparation

Allylsucrose is prepared by heating sucrose, sodium hydroxide, and allyl chloride in an autoclave at about 80° C. Allyl chloride is a cheap and abundant product prepared from a byproduct of petroleum distillation. After completion of the reaction (which takes a few hours), the product is purified by

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simple means. The autoclaves recommended for this process should be either stainless steel or glass-lined. The resulting product contains about six of the possible eight allyl groups and about two hydroxyl groups. The yield of allylsucrose is about 90%. The details of laboratory preparation have already been described (8, 9). At present, allylsucrose is being produced on a pilot-plant scale as part of a project sponsored jointly by the Eastern Regional Research Laboratory and the Sugar Research Foundation, Inc.

Allylsucrose containing five, six, seven or eight allyl groups has been described. Attempts to prepare triallylsucrose from one mole of sucrose and three moles of allyl chloride under our standard conditions resulted in a low yield of a hexaallylsucrose. An allylsucrose derivative containing only three polymerizable allyl groups, however, can be prepared as a mixed benzyl allyl ether. For industrial applications, allylsucrose with about six allyl groups is most practicable. Optimum conditions have been worked out for preparation of allylsucrose with either allyl bromide or allyl chloride.

Applications

Potential applications for allylsucrose include coatings for wood, metal or glass which are resistant to organic solvents, oils or heat; adhesives for glass or laminates; coating and impregnation of paper, textiles and other materials for improving the tensile strength and grease-proofing properties. New products with improved properties may result from copolymerization of allylsucrose with various monomers. Copolymerization with styrene gives a product having water resistance superior to that of allylsucrose itself; copolymerization with drying oils offers a method for upgrading drying oils. Other monomers, such as acrylates, methacrylates, maleates, maleic anhydride, crotonic acid, and acrylonitrile, may produce interesting copolymers. Useful alkyd resins may be obtained by the reaction of the free hydroxyl groups in allylsucrose with phthalic, fumaric, itaconic, and other dibasic acids. The free hydroxyls can react with urea formaldehyde and other resins.

Economics

Inasmuch as the work of the pilot plant has not been completed, it is impossible at present to give complete cost data for the process for preparing allylsucrose. It is possible, however, to give approximate data for materials cost, which will represent approximately 80% of the total cost of the product. At the present prices of sugar (\$0.0715/lb.), sodium hydroxide (\$0.0305/lb.), and allyl chloride (\$0.15/lb.), and on the assumption of a 90% yield of allylsucrose containing six allyl groups, the materials cost will be \$0.34 per pound of allylsucrose.

The cost of producing allylsucrose will vary considerably with variations in the price of raw materials. Thus, if the price of allyl chloride is reduced to \$0.12/lb. the materials cost of allylsucrose will be \$0.29/lb. On the basis of \$0.03/lb. for sucrose, allylsucrose will be \$0.315/lb. On the basis of reduced prices for both sucrose and allyl chloride, the materials cost for allylsucrose will be \$0.26/lb.

At present, 100% excess allyl chloride is used in the preparation of allylsucrose. At the end of the reaction, most of it has been transformed into diallyl ether; the rest is partly unused allyl chloride and partly allyl alcohol. Recovery of these three products will effect further savings in the cost of producing allylsucrose. Allyl alcohol has a market; allyl chloride goes back into the process. Diallyl ether has only potential uses, but it can be made into allyl chloride by a process developed by the Shell Development Company. Whatever the ultimate cost of producing allylsucrose might be, it is not expensive at present, and potentially it is a cheap material for industrial uses.

Polymerization

Allylsucrose is a sirupy viscous liquid of light yellow color. When deposited either as such or from a solution of organic solvent, the coating will be uneven and will remain tacky for days. In order to get a uniform coating, drying in a reasonably short time, allylsucrose must be partially polymerized, or blown, by heating it while passing air or oxygen through it. During blowing, a number of physical and chemical changes take place, some of which are recorded in Table I. Blown allylsucrose is always lighter in color than the original material.

Table I.-Changes During Blowing of Allylsucrose

Time (hours)	Refractive index at 25°C.	Viscosity at 100°C., centi- stokes	Peroxide number	% Allyl	%OH
0	1.4890	12	5.6	41.5	4.7
1	1.4920	36	128.8	39.8	4.9
1.5	1.4945	80	155.0	37.9	5.1
2.0	1.4960	250	164.0	37.0	5.1

Figure I shows changes in viscosity and refractive index during blowing of allylsucrose prepared in a stainless steel autoclave. Since the refractive index is the easier and the quicker determination of the two, it is used as a criterion to determine the desired degree of polymerization. For preparing coating solutions, we usually stop the blowing at the refractive index of 1.4950-1.4955 at 25°C. At this point, a film of this material deposited from a solution in an organic solvent (toluene, turpentine) will dry (in the presence of 0.1% of cobalt drier) free of tack in 60 to 90 minutes at room temperature and will completely polymerize in about a week. At 55°C. the film will cure in about 18 hours (without cobalt drier); at 110°C. it will cure in about 2 hours.

Various substances, besides paint drier, will hasten the polymerization of allylsucrose. Table II shows the affects of various esters of acrylic and methacrylic acids on the gelation time of allylsucrose.

FIG.1 POLYMERIZATION OF ALLYLSUCROSE AT 100° C

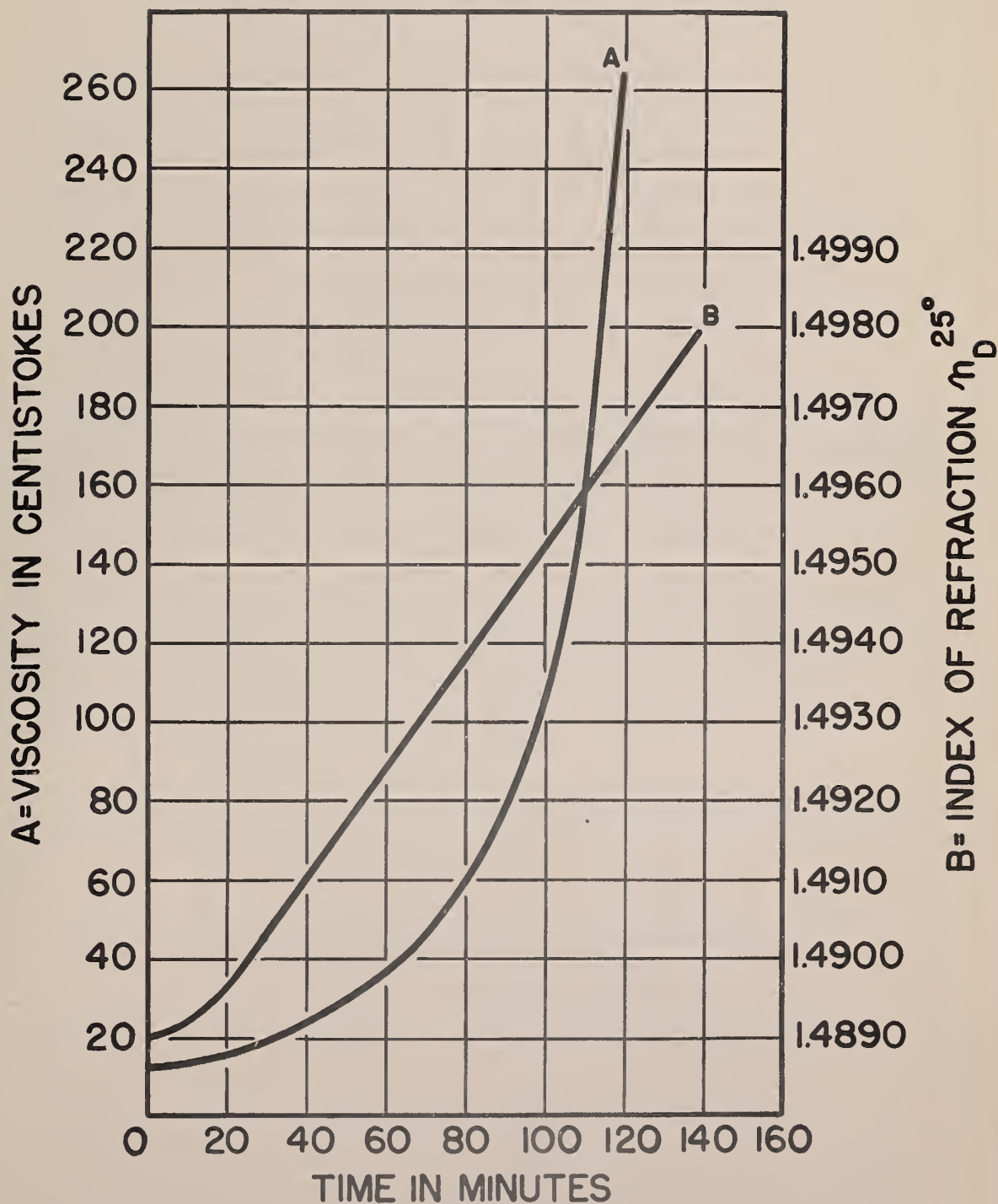


Table II.-Effects of Acrylic and Methacrylic Esters on Gelation of Allylsucrose at 100° C.

Allylsucrose + equal amount of:	Gelation Time (min.)
m Tollyl acrylate	210
Butyl methacrylate	135
Phenyl methacrylate	106
2-Ethyl hexyl acrylate	87
Octyl methacrylate	69
Cyclohexyl acrylate	51
Tetrahydrofurfuryl methacrylate	37
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Storage

Monomeric allylsucrose can be stored indefinitely at room temperature; blown allylsucrose ($n_D^{25} = 1.4955$) gels within a few days. Solutions of blown allylsucrose in an organic solvent, however, may be stored safely for long periods. Solutions containing driers may be stored if the container is completely filled.

Color

Allylsucrose is a light-yellow liquid; blown allylsucrose is somewhat lighter in color. According to Gardner's Color Standards for liquids, unblown allylsucrose falls within the range 3-7; a 50% solution of blown allylsucrose in toluene is in the range 2-3.

Viscosity

Solutions containing high solids content with relatively low viscosity can be prepared easily. The viscosity of the resulting solution depends largely on the type of solvent used (Table III)

Table III.-Viscosity of Allylsucrose in Various Solvents

Solvent	% Solids	Viscosity at 25°C. (Gardner-Holdt)	Stokes
Butanol	80	L	3.0
Toluene	80	H	2.0
Lacquer solvent ¹	80	H	2.0

¹ Composition of lacquer solvent (parts by weight): butyl acetate 6, ethyl acetate 1, butyl alcohol 2, ethyl alcohol 1, toluene 4.

Solubility

Table IV shows the solubility of allylsucrose in various solvents for the ratio 1 gram of allylsucrose to 10 cc. of solvent.

Table IV.-Solubility of Allylsucrose

Solvent	Blown or unblown material
Benzene	Soluble
Toluene	"
Xylene	"
Ethyl ether	"
n-Butyl ether	Insoluble
Carbon tetrachloride	Soluble
Chloroform	"
Ethyl acetate	"
Butyl acetate	"
Methyl, ethyl, or butyl alcohol	"
Acetone	"
Methyl ethyl ketone	"
Ethylene and diethylene glycol	Insoluble
Methyl or butyl cellosolve	Soluble
Methyl or hexyl carbitol	"
Nitroethane, nitropropane	"
Nitrobenzene	"
Hexane	Insoluble
Turpentine	Soluble

The solvents in Table IV are not equally effective. Among those which can hold high concentrations of allylsucrose are ketones, cellosolves, carbitols, toluene, xylene, turpentine and others.

Plasticizers

Although panels coated with allylsucrose have retained their original smooth surface and gloss for longer than 18 months, in general plasticizers or resins should be added to impart greater flexibility and thereby minimize cracking or crazing of films. Table V indicates the compatibilities of plasticizers studied up to the present. Paraplex RG 7 and Aroclor 1248 are the most effective of this group.

Table V.-Compatibility of plasticizers with blown allyl-
sucrose and allylsucrose monomer^{1, 2}

Plasticizer	Allylsucrose: plasticizer	Blown allylsucrose	Allylsucrose monomer
Aroclor 1248	1:1	C	C
	1C:3	C	C
Aroclor 1254	1:1	C	C
	1C:3	C	C
Aroclor 4651	1:1	C	C
	1C:3	C	C
	1C:1	C	C
Beckosol 1323	1:1	I	C
	1C:3	I	C
	1C:1	I	C
Dow X-565	1:1	C	C
	1C:3	C	C
Thiokol LP 3	1:1	C	C
	1C:3	C	C
	1C:1	I	I
Thiokol ZL 100	1:1	C	C
	1C:3	C	C
Paraplex RG-7	1:1	I	C
	1C:3	C	C
	1C:1	C	C
Paraplex G 50	1:1	I	I
	1C:3	I	I
	1C:1	I	C
Paraplex A1 16	1:1	I	C
	1C:3	I	I
	1C:1	I	I
Duraplex ND-77 B	1:1	I	C
	1C:3	I	I
	1C:1	I	I
Amino Silane RD-602	1:1	C	C
	1C:3	C	C
Amino Silane RD-611	1:1	I	I
	1C:3	I	I
	1C:1	I	I
Bakelite J1C433	1:1	I	I
	1C:3	I	I
	1C:1	C	C
Thiokol LP 2	1:1	I	I
	1C:3	I	I
	1C:1	I	I
Pittsburgh Plate Glass 178-16	1:1	I	I
	1C:3	I	I
	1C:1	C	C

¹ The mention of commercial products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over others of similar nature.

² C = compatible; I = incompatible.

Copolymerization with Styrene

Allylsucrose is well suited for applications that require resistance to organic solvents and heat: modified allylsucrose is required for uses demanding water resistance. By copolymerization with a cheap raw material - styrene - partially blown allylsucrose has been converted into a homogeneous product which gives clear films of improved resistance (10). Styrenated allylsucrose cured at 150° C. or air-dried, gives films with good water resistance, but films cured at 100° give superior over all solvent resistance. Table VI compares resistance of styrenated allylsucrose with that of allylsucrose itself.

Table VI.-Evaluation of Styrenated Allylsucrose

	Curing time, at 100° C., hrs.	Time of failure of the film (hours)				
		50% ethanol	4% acetic acid	5% sodium hydroxide	Dis- tilled water	Boil- ing water Ace- tone
Styrenated allylsucrose	2	>72	>72	48	>72	>12 >72
Blown allyl- sucrose	2	3	5	10 mins.	48	1 min. 15
Air-dried styrenated allylsucrose	<u>1</u> /	>72	6	3 mins.	72	>12 >72

¹ Dried to touch in 30 minutes; dried hard in 4 hours. Solvent resistance tests determined after standing at room temperatures for 2 weeks.

Derivatives

Since there is some evidence to support the belief that the free hydroxyl groups of allylsucrose are primarily responsible for water sensitivity, allylsucrose derivatives with substantially fewer hydroxyl groups were prepared. Among these were some esters, such as acetylallylsucrose and methacrylallylsucrose, and some ethers, such as ethylallylsucrose and benzylallylsucrose. Since study of these derivatives is only in the preliminary stage, we have little information about their properties and potential commercial utility.

Allylsucrose and Drying Oils

An interesting development which may lead to practical results is the copolymerization of allylsucrose with drying oils. At room temperature, allylsucrose is miscible with oiticica oil but immiscible with tung oil. With oils like raw and boiled linseed oil, dehydrated castor oil and soybean oil, it forms cloudy solutions. When mixtures of allylsucrose and any of the above-mentioned oils are blown with oxygen at 100° C., clear copolymers soluble in

organic solvents are obtained (11). With the exception of tung and oiticica oils, all drying oils dry more slowly than allylsucrose. Table VII gives gelation times for various oils and mixtures of oils and allylsucrose. These data clearly show that allylsucrose can be recommended as an upgrader for drying oils.

Table VII.-Gelation Times of Oils and Mixtures of Oils and Allylsucrose

Material	Gelation Time at 100°, min. ¹
Tung oil	121
Oiticica oil	136
Allylsucrose	168
Boiled linseed oil	455
Dehydrated castor oil	522
Raw linseed oil	947
Soybean oil	1275
50% boiled linseed oil + 50% allylsucrose	262
50% soybean oil + 50% allylsucrose	381
50% raw linseed oil + 50% allylsucrose	500
Soybean oil + 0.2% cobalt	367
50% soybean oil + 50% allylsucrose + 0.2% cobalt	131

¹ 7.2 cc. of material; 7.5 liters of oxygen per hour.

Summary

Allylsucrose, a potentially inexpensive material, can be prepared in good yield from sucrose and allyl chloride in the presence of sodium hydroxide. Various practical applications suggested by the properties of the polymerized product are indicated. At present, commercial development of allylsucrose appears to be the most direct approach to industrial utilization of sucrose.

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